



**U.S. Department of Energy**  
Livermore Site Office, Livermore, California 94550

---

**Lawrence Livermore National Laboratory**  
University of California, Livermore, California 94550



**SUMMARY REPORT  
ON THE SUBSURFACE CHROMIUM  
REDUCTION TREATMENT TEST AT  
RIVERBANK ARMY AMMUNITIONS PLANT**

*Author:*

**M. Ridley**

**May 2007**



**Environmental Protection Department**  
Environmental Restoration Division

UCRL-TR-231326



---

---

**SUMMARY REPORT  
ON THE SUBSURFACE CHROMIUM  
REDUCTION TREATMENT TEST AT  
RIVERBANK ARMY AMMUNITIONS PLANT**

*Author:*

**M. Ridley**

**May 2007**



**Environmental Protection Department**  
Environmental Restoration Division

## Table of Contents

<b>TREATMENT CONCLUSIONS .....</b>	<b>2</b>
TREATABILITY STUDY DESCRIPTION .....	2
TREATMENT RESULTS .....	2
CONCLUSIONS FOR SITE 17 .....	3
FUTURE RECOMMENDATIONS FOR USE OF SODIUM DITHIONITE.....	3
<b>APPENDIX A: SUMMARY OF THE TREATABILITY STUDIES FOR SUBSURFACE HEXAVALENT CHROMIUM REDUCTION AT THE SITE 17.....</b>	<b>4</b>
STATEMENT OF PROBLEM .....	4
TREATMENT OPTIONS .....	4
<b>TREATABILITY TESTS.....</b>	<b>6</b>
RIVERBANK ARMY AMMUNITION PLANT BACKGROUND INFORMATION .....	6
SITE 17 BACKGROUND .....	6
SODIUM DITHIONITE APPLICATION AT RBAAP .....	7
FEASIBILITY QUESTIONS .....	7
<b>EXPERIMENTS AND RESULTS .....</b>	<b>7</b>
1. IRON CONCENTRATIONS AND ACCESSIBILITY .....	7
2. SODIUM DITHIONITE STABILITY .....	8
3. BY-PRODUCTS FROM THE REDUCTION PROCESS .....	10
CONCLUSIONS.....	11
<b>REFERENCES.....</b>	<b>12</b>

## Treatment Conclusions

### Treatability Study Description

A treatability study was conducted at Riverbank Army Ammunition Plant's (RBAAP) Site 17, to evaluate the effectiveness of a permeable reactive barrier (PRB) for the treatment of hexavalent chromium ( $\text{Cr}^{6+}$ ). The chromium contamination at Site 17 is hydrologically isolated and unsuitable for standard extraction and treatment (pump and treat). The majority of the chromium contamination at Site 17 is trapped within the fine grain sediments of a clay/silt zone (45' to 63'). The PRB was established above and adjacent to the contaminated zone at Site 17 to reduce the hexavalent chromium as it leaches out of the contaminated clay/silt zone separating the A zone from the A' zone. Site 17 and the monitoring network are described in the *In-Situ Chromium Reduction Treatability Study Work Plan* (CH2MHILL, January 2004).

The PRB was created by reducing naturally occurring  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  with the injection of a buffered sodium dithionite solution into subsurface chromium source area. The  $\text{Cr}^{6+}$  leaching out of the contaminated clay/silt zone and migrating through the PRB is reduced by  $\text{Fe}^{2+}$  to  $\text{Cr}^{3+}$  and immobilized (Amonette, *et al.*, 1994). The sodium dithionite will also reduce accessible  $\text{Cr}^{6+}$ , however the long-term reductant is the  $\text{Fe}^{2+}$ . Bench scale tests (Appendix A) were conducted to assess the quantity and availability of the naturally occurring iron at Site 17, the ability of the sodium dithionite to reduce the hexavalent chromium and Fe within the sediments, and the by-products produced during the treatment. Appendix A, provides a detailed description of the laboratory treatability tests, and provides background information on the technologies considered as possible treatment options for Site 17.

Following the sodium dithionite treatment, groundwater/treatment solution was extracted to remove treatment by-products (sulfate, manganese, and iron).

The following sections briefly discuss the current treatment status, future recommendations for Site 17, and future recommendations for the application of sodium dithionite at additional sites.

### Treatment Results

- At the completion of the treatability test, none of the wells at Site 17 had detectable hexavalent chromium, but the sulfate, iron, and manganese concentrations were detected and exceeded the CA secondary drinking water standards.
- The extraction done after the injection of the sodium dithionite solution to remove the sulfate, manganese, and iron has to a large extent negated the effectiveness of the iron reduction. Riverbank's local groundwater is naturally high in dissolved oxygen (concentration range at Site 17: 1.8 to 6.0 mg/l) and moving this type of groundwater through the reduced zone caused oxidation of the  $\text{Fe}^{2+}$  within the treatment zone, followed by a new release of hexavalent chromium detected in one of the treatment wells.

## Conclusions for Site 17

- Additional extraction at Site 17 will continue to degrade the PRB, threatening to release additional  $\text{Cr}^{6+}$  into the groundwater. Sulfate and manganese only exceed the CA secondary drinking water standards in the area immediately surrounding the PRB. It is unlikely that these contaminants will threaten any water supply wells in the area.
- The chromium concentrations are increasing in IW-17. The current concentration is still only a third of the original concentration. It might be worth investigating some of the new zero valent iron treatments, such as nanoscale zero-valent iron (NZVI) to replace the in-situ naturally occurring iron, which may no longer be available for reduction. The NZVI has been successfully tested at NASA in Florida (O'Hara, 2006), and demonstrated no release of metals from the natural sediments. This might also be a viable option for other sites at RBAAP.

## Future Recommendations for Use of Sodium Dithionite

Sodium dithionite created PRBs for the reduction of chromium have been successfully tested at many sites (U.S. Coast Guard Support Center in Elizabeth City, Frontier Hard Chrome Site in Washington State, Macalloy Corporation Site in South Carolina, and Hanford Site in Washington State). Both Frontier Hard Chrome and Hanford Sites applied full-scale treatments. The Frontier Site was successfully closed. The Hanford Site experienced breakthrough in their reduction zone, most likely due to an insufficient amount of naturally occurring iron within the aquifer sediments. The Coast Guard Center is now is currently proposing to use a full-scale treatment after their successful *in-situ* pilot test using sodium dithionite for chromium reduction. Based on the successful applications at the other sites, the recommendations for future applications are:

- No extraction following the sodium dithionite treatment. None of the sites listed above extracted any groundwater/reactant solution after the treatment. The sulfate, manganese, and iron were not considered to be a concern.
- Add  $\text{Fe}^{2+}$  to the initial dithionite solution to augment the naturally occurring Fe. The addition of  $\text{Fe}^{2+}$  would allow less sodium dithionite solution to be used. The addition of ferrous sulfate ( $\text{FeSO}_4$ ) to the dithionite solution has been successfully tested at Macalloy Corporation Superfund site in North Charleston, SC (Su and Ludwig, 2006).

## Appendix A: Summary of the Treatability Studies for Subsurface Hexavalent Chromium Reduction at the Site 17

### Statement of Problem

There is hexavalent chromium ( $\text{Cr}^{6+}$ ) contamination located (45ft to 65ft) below ground surface (bgs) within a clay/slit lens between the A and A' zones at Site 17. The A zone is an unsaturated zone at a depth that varies between 29 to 60 feet, and its upper 15 feet is sandy loam and the lower 10 feet is predominately clay and silt. The A' zone, below the A zone, is partially to fully saturated, depending on the location, at a depth that varies from 60 to 90 feet bgs, and its lower 10 feet is predominately clay with thinly interbedded sand and silt.

The regulators consider Site 17 a source area for the A, and A' wells. The chromium contamination is typically detected in the A zone wells at Site 17 when the water table rises and leaches hexavalent chromium from the contaminated clay/slit lens into the A zone. The water levels in the area have been dropping for the last 5 years, and the A zone has been dry for several years. The chromium contamination is hydrologically isolated, which makes the hexavalent chromium difficult to extract and treat (pump and treat).

### Treatment Options

The treatment of  $\text{Cr}^{6+}$  contamination in sediment greatly depends on the location of the sediment. If the contamination is at the ground surface and/or shallow, then excavation and disposal of the sediment is an option. Depending on the amount of sediment, this can be very expensive (Dragun, 1997). In many instances, hexavalent chromium contamination is discovered many years after the leakage/discharge, and the  $\text{Cr}^{6+}$  has migrated into the subsurface sediment and the groundwater. The typical treatment for hexavalent chromium contamination in the groundwater is extraction and treatment. However, as stated earlier, it is not a viable option for Site 17.

To address the expensive cost of the pump and treat or the inaccessibility of the  $\text{Cr}^{6+}$  contamination, many new subsurface (*in-situ*) processes are being developed and tested:

- 1) Bioremediation. Bioremediation typically involves adding nutrients to the subsurface environment to increase the rate at which contaminants are biodegraded by indigenous organisms. In the case of chromium, a carbon source is injected to promote the *in-situ* microbial reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$ . The reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  produces a precipitate of  $\text{Cr}(\text{OH})_3$ . This precipitate has low solubility and is stable. The advantages of bioremediation are the low cost and potential ease of application. The disadvantages are the chromium needs to be readily available, and release of metals (iron, manganese, arsenic) during the process could produce undesirable water quality changes (Water Science and Technology Board, 2003).
- 2) Permeable reactive zero-valent iron (ZVI) filing walls. The iron filing permeable walls use zero valent iron to reduce the  $\text{Cr}^{6+}$  as it flows through the permeable zone (Blowes, Ptacek, and et al., 2000). This technology can have a very expensive installation cost and is only feasible in shallow aquifers.

- 3) Nanoscale zero-valent iron (NZVI). The zero-valent iron nanoparticles (“Ferragels”) can be easier to use than the iron filing walls and the remediation rates are up to 30 times higher (Ponder, Darab, and Mallouk, 2000). Ferragels are thought to be more effective because the higher surface area exposure contacts more contaminated material. This technology looks very promising, but needs more testing and development.
- 4) Electrokinetics. Electrodes, a cathode and anode, are introduced into the sediment and charged (Acar and Alshawabkeh, 1993). The charged particles (that are free to move) and ions are mobilized by the electrical current and move toward the electrodes. Some of the limitations of electrokinetics are:
  - The effectiveness is sharply reduced for sediment/wastes with a moisture content of less than 10 percent.
  - In unsaturated sediments, the addition of water could potentially wash contaminants out of the area of influence.
  - The presence of buried metallic or insulating material can induce variability in the electrical conductivity of the sediment.
- 5) Chemically created permeable reactive barrier (PRB). The chemically created permeable treatment zone is produced by injecting sodium dithionite into subsurface sediment down gradient of the  $\text{Cr}^{6+}$  contamination (Fruchter and Amonette, 1996). Sodium dithionite reduces sediment Fe from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . This treatment only works in iron rich sediments. It is the  $\text{Fe}^{2+}$  that reduces the  $\text{Cr}^{6+}$  in the groundwater as it passes through this treated zone. This treatment may not be a permanent solution because the reductive properties of this treatment only last as long as the  $\text{Fe}^{2+}$  concentrations are high enough to reduce the  $\text{Cr}^{6+}$  passing through the this zone. The time frame for the effectiveness of the reductive zone is dependent on the groundwater velocity, the  $\text{Cr}^{6+}$  concentration and the oxidizing materials in the groundwater ( $\text{O}_2$ ,  $\text{SO}_4$ , and  $\text{NO}_3$ ). Thus far, chemically created reductive barriers have only been used down gradient of a source. The concern related to direct reduction at the source contamination is a large displacement of contaminant, thereby releasing of  $\text{Cr}^{6+}$  into the surrounding groundwater system. Since the subsurface target zone being considered at RBAAP is unsaturated, displacement is not a major concern.

Of the technologies discussed above, only the sodium dithionite created PRB is feasible. The bioremediation cannot create a long-term effect to address the contamination in the clay/silt zone, the water table is too low to use electrokinetics, the contamination is too deep to install a ZVI filing wall, and the NZVI needs more testing and development. (Note: This assessment was originally performed in 2003, and at that time no successful subsurface test had been performed using the NZVI. This technology has now been successfully tested, however the site is quite different from the RBAAP environment, and would require further testing to determine its applicability.)



## Treatability Tests

### Riverbank Army Ammunition Plant Background Information

In 1942, the Army constructed the Riverbank Army Ammunition Plant as an aluminum reduction plant to supply military requirements. Aluminum reduction processing occurred until 1945. The electrolytic cells (or “pots”) were used in the reduction process and the spent cells were disposed of in the RBAAP landfill. The cells contained cyanide, which then leached into the groundwater. The cyanide is a byproduct produced during the reduction of aluminum. Starting 1951, the installation has manufactured steel cartridge cases for the Army and the Navy. Other manufactured products include grenades and projectiles, which the Army ships to other ammunition plants for loading operations. In the past, a hexavalent chromium solution was used in the manufacturing process.

In FY85, a preliminary assessment and site inspection identified the following sites: an industrial wastewater treatment plant, an abandoned landfill, and four evaporation and percolation ponds located north of the plant near the Stanislaus River. Chromium was detected in drinking water wells at residences west of the installation and as a result, EPA placed the installation on the NPL in 1990.

### Site 17 Background

At Site 17, the chromium has seeped into a 20 feet thick (45ft to 65ft) silty clay lens. The Cr<sup>6+</sup> distribution in the Site 17 Area is as follows:

Location	Lithology	Conc.(mg/kg)	Location	Lithology	Conc.(mg/kg)
IW-17-40'	Sandy loam	ND	MW-17-1-40'	Sandy silt	ND
IW-17-45'	Silty clay loam	0.194	MW-17-1-45'	Silty clay	0.296
IW-17-50'	Silty clay loam	0.444	MW-17-1-52'	Clay loam	0.345
IW-17-54'	Silty clay loam	0.195	MW-17-1-54'	Clay loam	0.294
IW-17-56'	Silty clay loam	0.283	MW-17-1-56'	Clay loam	0.269
IW-17-58'	Silty loam	ND	MW-17-1-58'	Clay loam	ND
IW-17-63'	Sandy clay	0.296	MW-17-1-62'	Clay sand	0.222

Location	Lithology	Conc.(mg/kg)	Location	Lithology	Conc.(mg/kg)
MW-17-2-40'	Silty sand	ND	MW-17-3-40'	Sandy loam	ND
MW-17-2-45'	Clay	0.345	MW-17-3-45'	Clay loam	0.319
MW-17-2-52'	Clay	0.123	MW-17-3-50'	Loam	0.172
MW-17-2-54'	Clay	0.174	MW-17-3-52'	Clay	0.163
MW-17-2-56'	Clay	ND			
MW-17-2-60'	Silt	0.246	MW-17-3-60'	Sandy Clay loam	ND
MW-17-2-62'	Silty clay	ND	MW-17-3-62'	Sandy Clay	0.196

Location	Lithology	Conc.(mg/kg)
MW-17-4-40'	Silty clay loam	ND
MW-17-4-45'	Silty clay	ND
MW-17-4-52'	Silty clay	ND
MW-17-4-55'	Sandy clay	ND
MW-17-4-60'	Silt	0.146
MW-17-4-62'	Sandy clay loam	0.196

## Sodium Dithionite Application at RBAAP

The goal of the treatment is to reduce the natural subsurface  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  on the top layer of the clay/silt lens (45' to 50') at Site 17. After the treatment, the  $\text{Fe}^{2+}$  will reduce the  $\text{Cr}^{6+}$  as it leaches from the clay/silt zone.

## Feasibility Questions

To determine if sodium dithionite is feasible for application at RBAAP, several questions need to be answered.

1. Is there sufficient in situ iron to reduce the chromium contamination? And what percentage of iron is accessible for reduction?
2. Is the sodium dithionite stable enough to reduce the area of interest? Sodium dithionite is considered very unstable (Amonette et al., 1994), and may only be able to treat a very small area if the chemical degrades too quickly.
3. What are the by-products produced as a result of the reduction process (what metals are released from the sediment)? How might this process degrade the surrounding groundwater quality?

Laboratory experiments were conducted to answer the above questions. All of the experiments were conducted using a buffered sodium dithionite solution. The buffering is necessary to ensure the pH remains above 6.5 during the reduction reactions. The buffering is done with a carbonate/bicarbonate mixture.

# Experiments and Results

## 1. Iron Concentrations and Accessibility

To answer the question if RBAAP has sufficient accessible iron, the distribution of iron in the clay/silt lens was assessed. The total iron concentrations ranged from 16,200 mg/kg in the sandy clay to 37,300 mg/kg in the clay sediment. Clay samples from Site 17 were reduced with a buffered 0.1M sodium dithionite solution. The clay material was chosen for the experiments, because the majority of the iron in the sediment was associated with the clay sediment. Initial testing prior to reduction detected no  $\text{Fe}^{2+}$  in the clay. Nine samples were tested and the amount

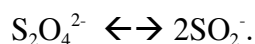
reducible iron ranged from 21.8% to 29.3% (average 25.5% or 9,525 mg/kg). Based on these results, there is in excess of 30,000 times more reducible iron than hexavalent chromium (average  $\text{Cr}^{+6}$  concentration is 0.3 mg/kg) contamination at Site 17.

In addition to testing the iron accessibility, the clay sediments were spiked with additional  $\text{Cr}^{6+}$  at 10 ppm and 100 ppm to assess the effectiveness of the  $\text{Fe}^{2+}$  reduction process. The  $\text{Fe}^{2+}$  completely reduced the hexavalent chromium and the reduction occurred within seconds.

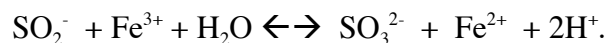
## 2. Sodium Dithionite Stability

Information related to the stability of sodium dithionite is very limited. Several reports suggest sediment and glass may affect the stability of sodium dithionite, but there is no research data to support those statements. What is known about sodium dithionite is that it is a very powerful, and fast reducing agent. The PRB is created by the following chemical reactions:

- I. The sodium dithionite ion dissociates by the following reaction:

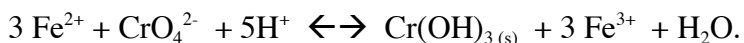


- II. The  $\text{SO}_2^-$  radical reacts with the oxidized iron in the sediment:

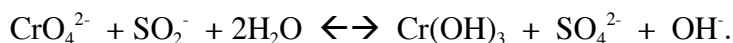


The reduced  $\text{Fe}^{2+}$  of the clay material remains within the sediment structure and does not go into solution. Reduction of the RBAAP clay detected 3.5 mg/kg release of iron or 0.03% of the reduced iron. This release of iron is most likely from the reduction of amorphous iron material not contained within the clay structure.

- III. The  $\text{Fe}^{2+}$  then reacts with the  $\text{Cr}^{6+}$  to produce chromium hydroxide:



If the dithionite is injected into the source of the chromium contamination, two reaction pathways will be available to reduce the  $\text{Cr}^{6+}$ . The first pathway will be the reduction by  $\text{Fe}^{2+}$ . The other pathway will be a direct reduction of  $\text{Cr}^{6+}$  by the dithionite:



The direct reduction of  $\text{Cr}^{6+}$  by the dithionite creates a precipitate of  $\text{Cr}(\text{OH})_3$  which is not bound to the surface of the sediment and remains in solution (Taylor et al., 2000). The  $\text{Cr}^{6+}$  reduced by  $\text{Fe}^{2+}$  is part of a sorption-reduction process and remains adsorbed to the surface of the sediment and does not go into solution.

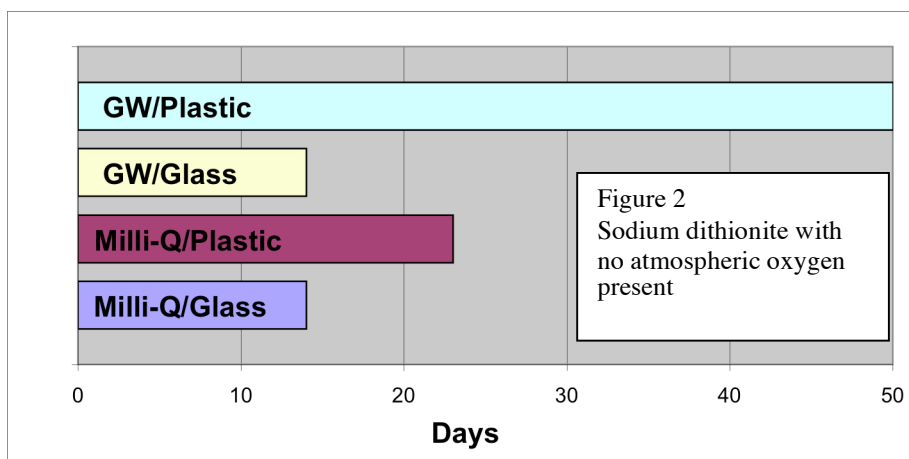
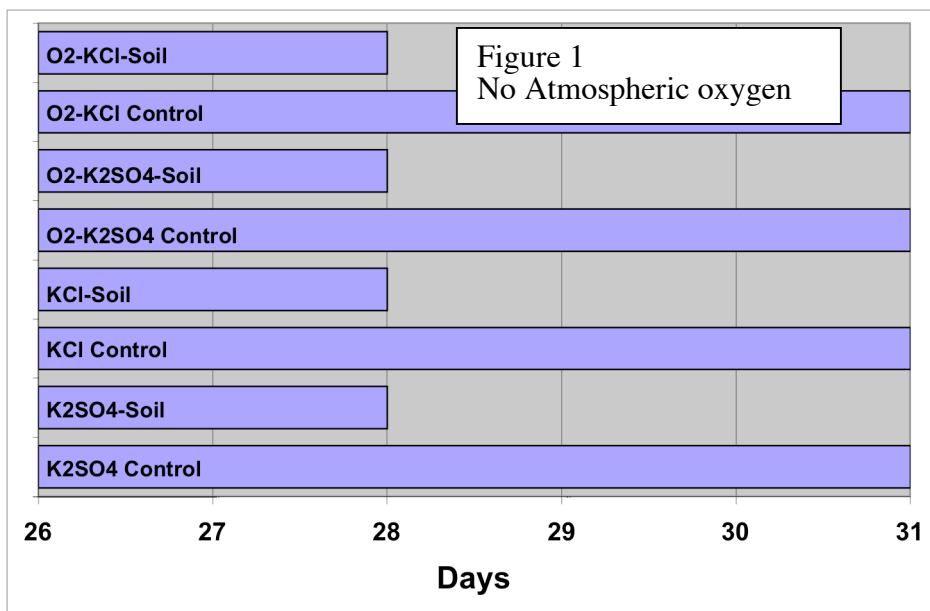
Dithionite can also undergo homogeneous and heterogeneous disproportionation reactions yielding  $\text{S}_2\text{O}_3^{2-}$ ,  $\text{HSO}_3^-$  and  $\text{H}^+$ . The Hanford treatability work suggested sodium dithionite could disproportionate when in contact with sediment by the following reaction:

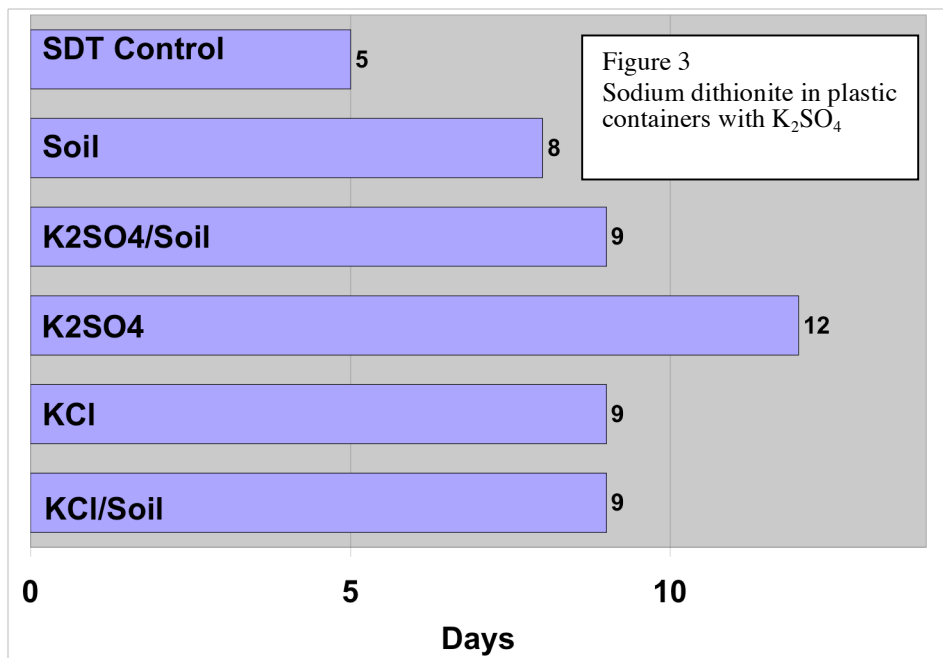


In examining the stability of buffered sodium dithionite, the following factors were tested:

- ◆ Oxygen
- ◆ Container material – glass and plastic
- ◆ Sediment material – clay
- ◆ Water – groundwater and ultra pure water
- ◆ Salt effects – KCl and  $K_2SO_4$

The significant finding from testing these factors was that the stability of sodium dithionite (SDT) is most impacted by exposure to atmospheric oxygen. Oxygen in the groundwater, and clay had little affect on the stability of sodium dithionite (Figure 1). Glass and ultra pure water demonstrated a strong effect (Figure 2) on sodium dithionite stability. In addition, adding  $K_2SO_4$  to the sodium dithionite solution delayed the degradation while exposed to atmospheric oxygen (Figure 3). The sodium dithionite solution was stable for 12 days in the presence of atmospheric oxygen with the addition of  $K_2SO_4$ , while sodium dithionite alone was stable for only 5 days.





### 3. By-products From the Reduction Process

By-products can be a major concern during an in situ reduction process. Not only do the by-products released into the treatment zone need to be considered, but also how these by-products react as they migrate outside the treatment zone. One such by-product typically released during a reduction process is manganese. Manganese in the  $Mn^{+2}$  state is of little consequence, however as the  $Mn^{+2}$  migrate from the reduced treatment zone to the naturally occurring oxidizing zone the  $Mn^{+2}$  will revert back to  $MnO_2$ . In reverting back to  $MnO_2$ , Mn will first become  $Mn^{+3}$  and this is known to be a strong  $Cr^{3+}$  oxidizer (Nico, 2000). In addition,  $MnO_2$  is known to oxidize arsenic (Ghurye, 2001). Therefore, this experiment examined the release of metals from the RBAAP sediment to determine what level of impact sodium dithionite might have on the aquifer.

Several RBAAP site sediment materials were used in the experiments. The sediments were reduced with a buffered sodium dithionite solution prepared using RBAAP groundwater. The only metals released during the reduction reaction were iron (11.6 mg/l), manganese (1.8 mg/l), nickel (0.059 mg/l) and total chromium (0.3 mg/l). The concentrations were the highest levels detected during the testing. These results are consistent with the pilot test results. The manganese levels were still high enough to recommend limited extraction of the reduced solution containing by-products to ensure no chromium or arsenic oxidation outside of the treatment area. In addition, extraction would be necessary after the reduction of the iron to reduce the levels of sulfate from the sodium dithionite. The sulfate is the end product of the sodium dithionite reduction reaction.

## Conclusions

Based on the results of the above experiments, the pilot test was conducted using a buffered sodium dithionite solution with  $K_2SO_4$  added. The results of the pilot test are discussed in the RBAAP Groundwater Monitoring Program – Quarterly Groundwater Monitoring Report.

## References

- Amonette, J. E., Szecsody, J. E., Schaef, H. T., Templeton, J. C., Gorby, Y. A., and Fruchter, J. S. (1994).** "Abiotic reduction of aquifer materials by dithionite: A promising *In-situ* remediation technology." Pacific Northwest Laboratory, Richland, WA.
- Blowes, D. W., Ptacek, C. J., Benner, S. G., McRae, C. W. T., Bennett, I. A., and Puls, R. W. (2000).** "Treatment of inorganic contaminants using permeable reactive barriers." *J. Contaminant Hydrology*, 45: 123-137.
- Dragun, J. (1997).** "Chromium in soil: Perspectives in chemistry, health, and environmental regulation." *Soil Contamination*, Lewis.
- Fruchter, J. S., and Amonette, J. E. (1996).** "In-situ redox manipulation field injection test report - Hanford 100-H Area." PNNL-11372, Pacific Northwest National Laboratories, Richland, WA.
- Ghurye, G., and Clifford, D. (2001).** "Laboratory study on the oxidation of arsenic III to arsenic V" EPA/600/R-01/021, University of Houston, Houston, TX.
- Nico, P., and Zasoski, R. J. (2000).** "Importance of Mn(II) availability on the rate of Cr(III) oxidation on d-MnO<sub>2</sub>." *Environ. Sci. Technol.*, 34(16): 3363-3367.
- Taylor, R. W., Shen, S., Bleam, W. F., and Tu, S.I. (2000).** "Chromate removal by dithionite-reduced clays: Evidence from direct X-Ray adsorption near edge spectroscopy (XANES) of chromate reduction at clay surfaces." *Clays and Clay Minerals*, 48(6): 648-654.
- U.S. EPA (2004).** "Frontier Hard Chrome long-term monitoring report Event 2- April 2004." RFW230-2A-AQIX. June 2004.
- Water Science and Technology Board (2003).** *Environmental Cleanup at Navy Facilities: Adaptive Site Management.* National Academy of Sciences.